

Comment on “Extreme lowering of the Debye temperature of Sn nanoclusters embedded in thermally grown SiO_2 by low-lying vibrational surface modes”

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This Comment corrects two separate errors which previously appeared in the calculation of vibrational mode frequencies of tin spheres embedded in a silica matrix. The first error has to do with the vibrational frequency of a free elastic sphere. The second error has to do with the effect on the vibrational frequencies of a sphere due to its embedding in an infinite elastic matrix.

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In a recent article¹, Koops *et al.* discuss the normal modes of vibration of spherical tin nanoparticles embedded in a glass matrix using an elastic sphere model. However, the analysis errs in two respects in calculating the frequencies of the vibrational modes.

The first issue has to do with the vibrational frequencies of a free sphere, referred to here as the free sphere model (FSM). Specifically, the frequency for the breathing mode is often obtained incorrectly because of the misapplication of a formula that is only applicable to modes with angular momentum $\ell > 0$. This error is recurrent in the literature.^{2,3} Some authors have since corrected them.^{4,5}

The second issue has to do with the vibrational frequencies of an elastic sphere embedded in an infinite elastic matrix, referred to here as the complex frequency model (CFM) since the transmission of vibrational energy out into the matrix leads to temporally de-

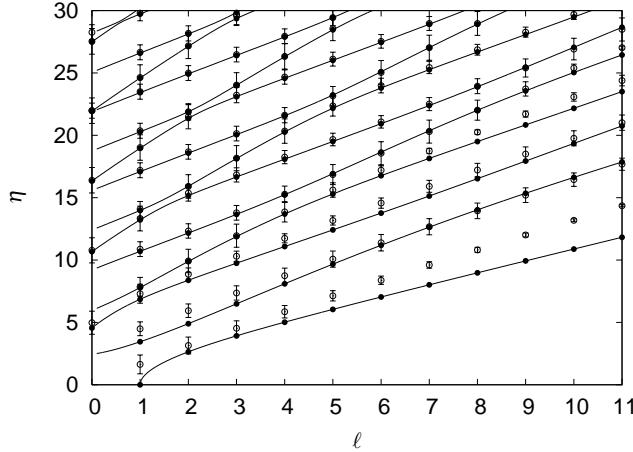


FIG. 1: Corrected spheroidal FSM (solid line with filled circles) and CFM (open circles show real part, bars show half width at half maximum due to imaginary part of frequency) dimensionless mode frequencies for a tin nanoparticle in a silica matrix versus angular momentum ℓ . CFM matrix modes are not plotted

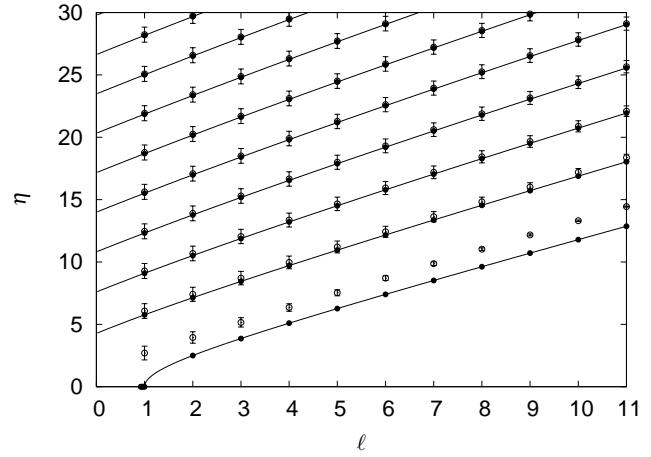


FIG. 2: Corrected torsional FSM (solid line with filled circles) and CFM (open circles show real part, bars show half width at half maximum due to imaginary part of frequency) dimensionless mode frequencies for a tin nanoparticle in a silica matrix versus angular momentum ℓ . CFM matrix modes are not plotted

ing vibrational amplitude within the nanoparticle, which is described with a frequency with a nonzero imaginary part. The original solution of the problem was correct⁶ and an explanation is available elsewhere.⁷ This error results in incorrect estimates of the vibrational frequencies of the acoustic phonon modes of the tin nanoparticle in a glass matrix.

Figure 1 shows the corrected FSM and CFM frequencies for the spheroidal modes of a tin sphere. There are some additional CFM modes (not plotted in the figures) with large imaginary parts. These are called matrix modes.⁷ Koops *et al.* and others have added straight lines connecting the values of η for consecutive integer values of ℓ , so as to attempt to indicate families of modes. Instead, we have extended the FSM calculation of η to non-integer ℓ .⁸ This could also have been done for the CFM frequencies, but those lines are not shown. The CFM frequencies apply to the case of a silica matrix. The speeds

of sound for the tin nanoparticle and the silica matrix are as in Koops *et al.* Figure 2 shows the corresponding frequencies for the torsional modes.

Some past works^{9,10} have calculated the vibrational frequencies of a sphere embedded in an infinite matrix. It is traditional to describe these vibrations as “confined phonons”, however vibrations of the nanoparticle will be mechanically coupled to the glass matrix. Consequently, energy in the form of outward travelling waves will carry energy away from the nanoparticle, and result in the amplitude of the vibrational energy decreasing with time, implying exponential decay as well as both real and imaginary solutions for the frequency. Those earlier works found only real-valued frequencies for the vibrations. This does not make sense for modes which are evidently damped. The error in the earlier derivation is due to unrealistic boundary conditions which were chosen to be standing waves.^{9,11} However, as just mentioned, the physically appropriate boundary conditions should be outward travelling waves if the vibrational mode is considered to be confined within the nanoparticle.

The same conclusion can be reached by using the Core Shell Model (CSM) approach.⁷ In CSM, the nanoparticle of radius R_p is surrounded by a spherical matrix with finite outer radius R_m . The limiting case of $R_m \gg R_p$ is

studied in order to approach the situation of an infinite matrix. All normal modes of the system as a whole can be found, and all frequencies are real valued. In this situation, when the macroscopic limit of a large matrix is taken, mode frequencies are no longer discrete. However, for normalized modes, the squared displacement within the nanoparticle interior peaks near frequencies which correspond closely to the real parts of CFM frequencies. In addition, the half widths at half maximum (HWHM) of these peaks correspond closely to the imaginary parts of CFM frequencies. As a result, the understanding of the “confined” acoustic phonons in the nanoparticle has been confirmed from two quite different theoretical points of view.

In particular, it is important to note that the lowest frequency vibrational mode of a nanoparticle is not the breathing mode (the mode with purely radial oscillation). Rather, it is a mode with angular momentum $\ell = 2$. With both of the errors now resolved, it is essential to note that the lowest mode is the torsional $\ell = 2$ mode, whose displacement field has zero divergence, and that the next lowest mode is the spheroidal $\ell = 2$ mode.

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